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Applied: July 31, 1989 Application No.: H1-199918 Laid-Open: March 20, 1991

Kokai No.: H3-65532

Kokoku Date: March 1, 1995

TITLE: Crystallized glass having luster

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REFERENCES: JP Kokai (A) 63-303831, JP Kokai (A) 63-20134, JP Kokai (A) 58-

135156, JP Kokoku (B1) 51-38730, and "Glass Engineering Handbook" edited by Moritani et. al., Asakura Shoten, 48-6-20P,

585-589.

### 1. TITLE OF INVENTION

Crystallized glass having luster

### 2. REGION OF PATENT REQUESTED

#### Claim 1

Crystallized glass having luster which is characterized by a light transmissive crystallized glass having a linear expansion coefficient of -3 to -5  $\times$  10<sup>-7</sup>/°C of which surface is coated with a luster color film of at most 1  $\mu$ m in order to have the IR transmittance of 12% to 87% and the visible light transmittance of 1.7% to 69%.

### 3. DETAILED EXPLANATION OF INVENTION

## Industrial Application Fields

The present invention relates to the crystallized glass having luster which covers the light transmissive crystallized glass sheet with a luster color coating film so that it can be applicable as a part for an electric appliance and a heating apparatus.

### Conventional Techniques.

Light transmissive crystallized glass comprising low expansion crystals is a dense crystal form. It has a superior mechanical strength, thermal shock resistance, and chemical durability, in addition to its light transmission characteristics, therefore, it has been applied to various types of electric appliances and heating apparatuses. Further, in order to correspond to the customers' needs of higher quality and wider variety, it has been applied with a coating film so that it can further provide properties of decoration, light shielding, masking, and reinforcement, while maintaining the transparency. For example, JP Kokai 61-168586 discloses the formation of an inorganic coating film on the surface of the transparent heat resistance ceramics.

In addition, the materials for the luster colors combine noble metal elements and base metal elements in a diluted solution of organic compounds, which can form inorganic coating films through sintering. Therefore, they are widely employed for the decoration of china and glass (but not for crystallized glass).

### Problems Solved by the Present Invention

By utilizing the transparency of the transparent crystallized glass, there have been always customers' needs to apply various coating films for the addition properties of decoration, light shielding, masking, and reinforcement. However, when the sintering temperature of the coating film is at most about 900 °C, the transparent crystallized glass having a low linear expansion coefficient of -3 to -5 × 10°/°C covered with the coating film formation materials which comprise glass flux and ceramic paints may lead to a high decoration effect with a luster if the fusion between them has been achieved. However it is not suitable for the practical use since the cracks are generated on the coating film surface. On the other hand, when these materials do not fuse together, then cracks will not be generated, while its surface remains rough without density and luster. Therefore this type was suitable only for the very limited designs and functionalities.

The present invention aims to offer the crystallized glass having luster with a superior design and functions, which maintains the mechanical strength, thermal shock resistance and chemical durability as well as becomes suitable for decoration, light shielding, masking and reinforcement applications, by combining the transparent crystallized glass and luster colors.

### Methods to Solve Problems

In order to achieve the said purpose, the present invention offers the crystallized glass having luster which is characterized by the light transmissive

crystallized glass having a linear expansion coefficient of -3 to -5  $\times$  10<sup>-7</sup>/°C of which surface is coated with a luster color film of at most 1  $\mu$ m.

#### **Effects**

In the said constitution, the materials for the luster color combine noble metal elements and base metal elements within the diluted solution of organometallic compounds. And they form inorganic coating films by burning themselves onto the transparent crystallized glass. The coating film of the luster color is a transparent film of at least 1 µm thickness formed by metal oxide fine particles, therefore, the effects of the expansion coefficient difference from the low expansion crystallized glass is practically nonexistent. As a result, its thermal shock resistance and mechanical strength will not be impaired. Therefore, the selection of luster pastes may be carried out without considering the linear expansion coefficient of the luster. Thus a wide variety of metal elements may be selected and a wide variety of the customers' need for the design and functions can be responded.

Below, Examples are interpreted.

### Examples

Major raw materials of crystallized glass are Li<sub>2</sub>O<sub>1</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> and these are further mixed with crystal nucleation agents such as ZrO<sub>2</sub> and TiO<sub>2</sub>, and other additives at small amounts. The mixture is made molten at the temperature of about 1700 °C and formed into a flat sheet product by, for example, the roll method. Then the material glass is prepared after annealing to eliminate its distortion. The heat treatment of this material glass at about 900 °C grows  $\beta$ -quartz type crystals around the crystal nuclei, and a transparent crystallized glass having a linear expansion coefficient of -3 to -5 x 10<sup>-7</sup>/°C (below it is called N-O) is formed.

Selected luster pastes are LU-1007D, LU-1008D, LU-1404D, LU-1603D. LU-5500, SL-900X, and SL-900X-3 (all the above are product names). These comprises noble metal elements of gold, silver, platinum, palladium, and base metal elements are one or at least two of the following: bismuth, iron, cobalt, titanium, tin, chromium, nickel, silicon, magnesium, calcium, and lead. These pastes are coated on the N-O sample of a 3 mm thickness and 100 mm square in size by using the 250 mesh screen print method, and burnt on at 830 °C after drying.

The N-O samples applied with luster coating films are examined with an impact test which measures the destruction height of the 84 g rigid ball by dropping it from various heights. The result showed the average height for the

destruction of the samples was about 16 cm. On the other hand, the similar test was carried out for the N-O sample without a luster coating film. This result was also about 16 cm and the characteristics for both did not differ much.

Then, the N-O samples with luster coating films were heated to 720 °C and quenched by dropping them into 20 °C water. In this test, both the N-O samples with luster coating films and without a luster coating film did not show any fracture, breakage and cracks, and again their characteristics were almost the same. Further, apparent color, IR transmittance (measured by Hitachi Infrared Spectrophotometer 260-30), and visible transmittance (measured by Nippon Denshoku Kogyo Digital Colorimeter NDH-20D) were measured and the results are summarized in Table 1. The coating film surface presents metallic luster and is also dense and smooth.

Table 1

Luster Type	Apparent	IR Transmittance (%)		Visible
	Color	4000 cm <sup>-1</sup>	2800 cm <sup>-1</sup>	Transmittance (%)
LU-1007D	Transparent Gold Brown	79	64	66 - 69
LU-1118D*N1	Dark Blue	75	63	46 - 50
LU-1404D	Black	60	54	13 - 15
LU-1603D	Red Brown	87	67	36 - 38
LU-5500D*N2	Copper*1	75	59	16 - 17
LU-900X*N3	Black	12 '	16_	1.7 - 2.2
LU-900 X-3-N4	Dark Black	32	26	1.8 - 2.2
None		85	67	89.7

<sup>\*1</sup> The color through the N-O layer thickness is dark blue.

### Notes from Translator:

- \*N1 The product code should be corrected to LU-1008D, according to the text.
- \*N2 The product code should be corrected to LU-5500, according to the text.
- \*N3 The product code should be corrected to SL-900X, according to the text.
- \*N4 The product code should be corrected to SL-900X-3, according to the text.

Based on these results, the color, IR transmittance, and visible transmittance differ depending upon the luster types and they may be applied and combined accordingly.

### Concrete Example 1

A back surface (inner surface) of a flat sheet of the said transparent crystallized glass of a thickness of about 3 mm and 350 mm x 350 mm in size was print coated with a luster paste SL-900X-3 and a coating film was formed after sintering at 830 °C. As a result, the flat sheet having the properties listed in Table 1 was obtained. It is a suitable quality for the top plate of an electromagnetic cooking apparatus and its dense and smooth coating film surface eliminates the problems such as vapor adhesion and care after adhesive installation. Further, the surface where the coating film was formed was not intended for a severe wear, therefore it is suitable for the practical application.

### Concrete Example 2

A flat sheet of the said transparent crystallized glass with a thickness of about 3 mm and 350 mm x 350 mm in size was print coated with a luster paste LU-1603D and a coating film was formed after sintering at 830 °C. As a result, the flat sheet having the properties listed in Table 1 was obtained. It is a superior flat sheet which effectively cuts the visible light but can highly transmit the IR heat source, therefore, it is extremely suitable for the halogen heater application. The coating film may be or may not be formed on the top surface.

### Effects of Invention

The present invention can offer the crystallized glass having a luster color with a superior design and functions, which is a smooth, lustrous, and dense coating film, maintains the mechanical strength, thermal shock resistance and chemical durability of the transparent crystallized glass itself, and further is highly suitable for decoration, light shielding, masking and reinforcement purposes, thus suitable for various needs of customers, by combining the transparent crystallized glass and luster colors.